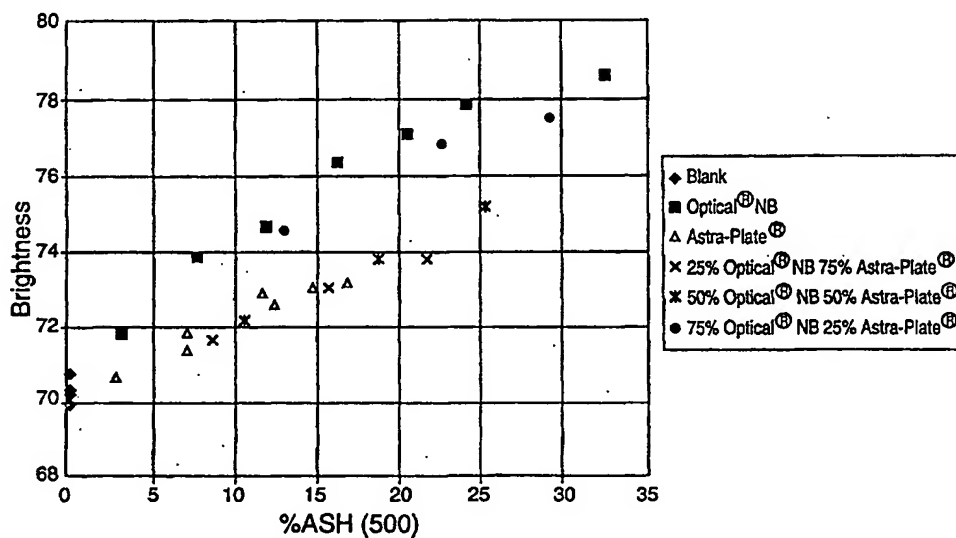




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C09C 1/02, 1/42, 1/62, 1/64, C04C 14/00, D21H 17/64, 17/68, 17/63, 17/67		A1	(11) International Publication Number: <b>WO 98/56860</b>
			(43) International Publication Date: 17 December 1998 (17.12.98)
(21) International Application Number: PCT/US98/11626		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 11 June 1998 (11.06.98)		Published With international search report.	
(30) Priority Data: 08/873,661 12 June 1997 (12.06.97) US			
(71) Applicant: ECC INTERNATIONAL INC. [US/US]; Suite 300, 100 Mansell Court East, Roswell, GA 30076 (US).			
(72) Inventors: RODRIGUEZ, Jose, M.; 107 Whippoorwill Court S.E., Eatonton, GA 31024 (US). FORRESTER, C., Dewey; 19844 N.E. 124th Place, Woodinville, WA 98072 (US).			
(74) Agent: KIKEL, Suzanne; ECC International Inc., Calgon Center, 5400 Campbells Run Road, Pittsburgh, PA 15205-1084 (US).			

(54) Title: FILLER COMPOSITION FOR GROUNDWOOD-CONTAINING GRADES OF PAPER



(57) Abstract

A blend of an acid tolerant precipitated calcium carbonate and a platy kaolin clay is used as a filler in uncoated calendered groundwood grades of paper, such as that used in newspaper inserts, magazines, and catalogues, in order to improve the optical and physical properties, such as opacity, brightness, and porosity, of the final paper product. The amount of the acid tolerant precipitated calcium carbonate and the platy kaolin clay range from 5 % to 95 %, by weight, per amount of filler used in the paper stock furnish, and more particularly from 25 % to 75 %, by weight, per amount of filler used in the paper stock furnish. The filler loading levels range from 1 % to 40 %, by weight, based upon the total weight of the paper stock furnish. The paper product may have a brightness ranging from 70 % to 80 %, and an opacity of 85 % to 95 %.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

-1-

"FILLER COMPOSITION FOR GROUNDWOOD-CONTAINING GRADES OF PAPER"  
BACKGROUND OF THE INVENTION:

This invention relates generally to the manufacturing of paper and in particular to a filler composition for use in  
5 uncoated groundwood-containing grades of paper for improving the optical and physical properties of the paper.

It is well-known in the paper industry that a wide variety of pigments, such as titanium dioxide, ground or precipitated calcium carbonate, talc, synthetic silicates, and  
10 clays, such as bentonite and kaolin, are suitable for use as paper fillers and/or coatings. Kaolin, a naturally occurring hydrated aluminum silicate, is presently the most widely utilized, especially as a filler material in the preparation of alkaline to weakly acidic paper in order to improve the  
15 optical properties, such as brightness, opacity, sheet gloss, and print gloss, and is available in a range of particle sizes and brightness. Calcium carbonate, particularly precipitated calcium carbonate, is increasingly being used particularly as a filler material in the making of alkaline  
20 paper. However, generally calcium carbonate cannot be used as a filler in acidic paper because of its low acid-resistance, causing it to decompose in an acidic environment.

Calcium carbonate is not used as a filler material in grades of paper containing groundwood in that this type of  
25 paper is acidic. Groundwood-containing grades of paper can be classified as newsprint, telephone directory paper, supercalendered paper, and soft-nip-calendered paper, all of which generally are uncoated. The end uses of supercalendered grades include newspaper inserts, magazines, and catalogues.  
30 The supercalendered (SC) grades are divided into SC-A, SC-B, and SC-C. SC-A is known to have a sheet brightness between 68-74%, sheet gloss between 30-40%, ink gloss between 20-30%, and filler levels between 15 to 30%. SC-B is known to have a sheet brightness between 65-70%, sheet gloss between 25-30%,  
35 ink gloss between 20-30%, and filler levels between 5 to 15%.

-2-

SC-C is known to have a sheet brightness between 62-65%, sheet gloss between 20-25%, ink gloss between 20-30%, and filler levels between 0 to 5%. Examples of patents which disclose calendering, supercalendering, and hot soft nip calendering (HSNC) include U.S. Patent Nos. 3,647,619; 4,624,744; and 4,749,445. U.S. Patent No. 3,647,619 explains that "supercalendering" refers to a process in which a web of paper is passed between the nip defined by a non-resilient roll, such as a roll of cast iron or steel, and a resilient roll such as a rubber-faced roll or a cotton fiber-filled roll to impart a uniform caliper and surface finish to the paper. Typically, a supercalender will comprise alternate resilient and non-resilient rolls arranged in a vertical stack or a non-resilient master roll with two or more resilient rolls positioned at space intervals about the periphery of the master roll. Supercalenders are normally utilized "off machine", i.e. supercalendering is usually carried out independently of the paper making process as a separate operation.

As stated hereinabove, presently, the platy kaolin clays have been the pigment of choice as a filler in these supercalendered grades in that, as a filler, these platy clays tend to increase smoothness, brightness, and opacity, and decrease the porosity of the sheet. The calcium carbonate pigment, however, offers a better brightness and a better opacity compared to the platy clays but tends to increase the porosity of the sheet, particularly when the sheet is supercalendered, which may be an undesirable physical property. Additionally, calcium carbonate can not be used in groundwood-containing grades of paper as these are considered as being acidic and, as stated hereinabove, the calcium carbonate tends to breakdown or decompose under acidic conditions.

-3-

Ideally, it is desirable to obtain the better optical values of the calcium carbonate and the better physical properties of the kaolin clay in a groundwood-containing grade of paper, particularly one which is supercalendered.

5       The advent of an acid tolerant precipitated calcium carbonate has made it possible to exploit the use of calcium carbonate filler material in a blend with platy kaolin clays in an acidic paper. Examples of an acid tolerant precipitated calcium carbonate are disclosed in U.S. Patent No. 5,531,821  
10 owned by the same assignee as the present application, and also in recently allowed patent applications bearing U.S. Serial Nos. 08/518,763, 08/518,652 and 08/546,222, and in pending patent applications bearing U.S. Serial Nos. 08/546,493, 08/614,863 and 08/546,145, also owned by the  
15 assignee of the present application. U.S. Patent No. 5,531,821 discloses the use of treating the calcium carbonate with an anionic salt and a cationic salt.

As discussed hereinabove, it is well known to incorporate clay-based filler compositions into the paper web during the  
20 formation of paper sheet to significantly improve the optical properties of the resultant paper sheet, such as brightness, opacity, sheet gloss, and print gloss. The improvement in opacity is the result of increased light scattering due primarily to the differences in indices of refraction between  
25 the filler, the paper fiber, and air, and to the increased number of light scattering voids formed in the paper web upon the incorporation of a clay filler. In order for the clay filler to perform well in improving opacity of the paper, the particle size distribution of the clay filler must be such  
30 that a large percentage of the clay particles have equivalent spherical diameters (e.s.d.) of between 0.6 and 1.5 microns and contain minimal particles with equivalent spherical diameters larger than 45 microns. It has become customary in the industry to beneficiate the crude kaolinitic clays used in  
35 a clay filler composition for paper making to improve particle

-4-

size distribution and color characteristics by removing ferric iron-containing compounds in the clay. U.S. Patent No.

4,650,521 discloses a process for treating a crude kaolinitic clay mineral under acidic conditions to provide a paper filler  
5 having improved color and G.E. brightness of about 85 to about 86.

Various commercial coating clays for paper are marketed by ECC International Inc., the assignee of the present application. An example is the ASTRA-PLATE® coating clay,  
10 which is characterized as a fine particle size, uncalcined delaminated kaolin clay. Astra-Plate® is a premium clay with a G.E. brightness of about 88.4. This product can also be used as a paper filler.

Coating compositions comprising blends of clays are well-  
15 known in the art. For example, a coating composition comprising a blend of kaolin clays is disclosed in U.S. Patent No. 5,085,707 to William M. Bundy, et al., formerly assigned to Georgia Kaolin Company, Inc. and presently assigned to the assignee of the present invention. Blends of clays for a  
20 filler composition for either alkaline or acidic paper may be known in the art. Blends of calcium carbonate, such as precipitated calcium carbonate and ground calcium carbonates are well-known in the art as filler material in the preparation of alkaline to weakly acidic paper. However,  
25 there is no disclosure known to the inventors of using a filler composition comprising a blend of kaolin clay and calcium carbonate to produce the desired optical and physical properties in the preparation of an acidic paper, such as those grades of paper containing groundwood.

30 SUMMARY OF THE INVENTION:

The present invention relates to a filler composition comprising a blend of platy clays and an acid resistant precipitated calcium carbonate for groundwood-containing grades of paper, which generally are made under acidic  
35 conditions.

-5-

More particularly, the invention is directed to a filler composition comprising an effective amount of an acid resistant precipitated calcium carbonate and a platy kaolin clay to produce a final end product exhibiting improved properties. The acid resistant precipitated calcium carbonate may range from about 5% to 95%, by weight, and the kaolin clay may range from about 5% to 95%, by weight, per amount of filler composition and, preferably, about 25% to 75%, by weight, of an acid resistant calcium carbonate and about 25% to 75%, by weight, of a platy kaolin clay per amount of filler composition. The end product may be a calendered grade or a supercalendered grade, such as SC-A, SC-B, or SC-C, and used as newspaper inserts, magazines, or catalogues.

It has been found that the use of a blend of platy kaolin clay with acid tolerant precipitated calcium carbonate offers an increase in opacity and in brightness, and a decrease in porosity in groundwood containing grades of paper.

It is an object of the present invention to provide a filler composition which improves the optical and physical properties of an acid-made paper.

It is a further object of the present invention to provide a paper product having enhanced optical and physical properties prepared using the filler composition of the present invention.

It is a still further object of the present invention to provide a process for the preparation of the aforesaid filler composition.

A still further object of the present invention is to provide a filler composition used in groundwood-containing grades of paper in the paper making systems.

BRIEF DESCRIPTION OF THE DRAWINGS:

FIGURE 1 shows a plot of TAPPI brightness (% Abs.) as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

-6-

FIGURE 2 shows a plot of TAPPI opacity (%) as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

5       FIGURE 3 shows a plot of Gurley porosity (sec/100 ml) as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

10       FIGURE 4 shows a plot of OpTest Formation Index as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

15       FIGURE 5 shows a plot of caliper (mills) as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

20       FIGURE 6 shows a plot of bulk (cm<sup>3</sup>/g) as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

FIGURE 7 shows a plot of sheet gloss (%) as a function of percent filler (ash at 500° C) for several different kinds of handsheets including those containing the filler composition of the present invention.

25       FIGURE 8 shows a bar graph of the TAPPI brightness (% Abs.) values obtained in a trial for several types of manufactured papers which include the filler composition of the present invention.

30       FIGURE 9 shows a bar graph of the TAPPI opacity (%) values obtained in the trial for several types of manufactured papers which include the filler composition of the present invention.

FIGURE 10 shows a bar graph of the tensile index values (Nm/g) in the machine direction for several types of



-7-

manufactured papers obtained in the trial and which papers include the filler composition of the present invention.

FIGURE 11 shows a bar graph of the tensile index values (Nm/g) in the cross direction for several types of manufactured papers obtained in the trial and which papers include the filler composition of the present invention.

FIGURE 12 shows a bar graph of the air permeability (Bendtsen, ml/min) values obtained in the trial for several types of manufactured papers which include the filler composition of the present invention.

FIGURE 13 shows a bar graph of the Gurley porosity (sec/100 ml) values obtained in the trial for several types of manufactured papers which include the filler composition of the present invention.

FIGURE 14 shows a bar graph of the gloss (%) values obtained in the trial for several types of manufactured papers which include the filler composition of the present invention.

DETAILED DESCRIPTION OF THE INVENTION:

The filler composition of the present invention comprises (a) a platy clay and (b) an acid tolerant precipitated calcium carbonate, and is particularly useful in uncoated groundwood-containing grades of "acid" made papers, such as newsprint, telephone directory paper, supercalendered paper, or soft-nip calendered paper. Thus, the filler composition of the present invention has particular utility in the manufacture of supercalendered (SC) paper grades which are divided into SC-A, SC-B, and SC-C, and whose end use includes newspaper inserts, magazines, and catalogues.

More particularly, the instant invention is directed to a filler composition for a groundwood-containing grade of paper comprising a mixture of an acid resistant precipitated calcium carbonate and a platy kaolin clay to produce a final end product exhibiting improved physical and optical properties.

The instant invention is further directed to a process for improving the optical and physical properties of a paper

-8-

web comprising the steps of forming a web of papermaking fibers including groundwood and a filler composition comprising an effective amount of an acid resistant precipitated calcium carbonate and an effective amount of a platy kaolin clay to produce an acid type final product.

The instant invention is further directed to improved acid-made paper products containing the filler composition of the present invention and to a method of preparing the same comprising adding to a papermaking stream an effective amount of an acid resistant precipitated calcium carbonate and an effective amount of a platy kaolin clay.

The effective amount of the components comprising the filler composition of the invention is that amount necessary to improve the optical and physical properties of the paper and are from about 5% to about 95%, by weight, for the acid resistant calcium carbonate and the platy kaolin clay and, preferably, from about 25% to about 75%, by weight, for the acid resistant calcium carbonate and from about 25% to about 75%, by weight, for the platy kaolin clay per amount of filler composition.

The percentage of the two components of this blended filler preferably ranges from about 5% to 95%, by weight per amount of filler. The filler composition of the invention was used as a paper filler to produce handsheets containing amounts ranging from about 1.0% to about 40% blended filler as shown in Figures 1-7.

As used herein, the term "acid resistant calcium carbonate" refers to treated calcium carbonate that can be used in a papermaking process having a pH below 7.5.

As used herein, the term "platy kaolin clay" refers to clay with a high aspect ratio, of about 30 to about 40.

As used herein, the term "acidic made paper" refers to paper made in the pH range of 5.0 to 7.0.

An example of a platy kaolin clay which may be used in the present invention and which is marketed as either a

-9-

commercial coating or filler clay is the ASTRA-PLATE® clay product. This product was originally manufactured by Georgia Kaolin Company, Inc. of Union, N.J., and is presently being manufactured by ECC International Inc., Sandersville, GA, the present assignee of this trademark and of the present application. ASTRA-PLATE® is a fine particle size, uncalcined, undefined, delaminated kaolin clay. The typical physical properties of ASTRA-PLATE® are: a G.E. brightness of about 88.4; a pH of about 6.9; a particle size distribution of at least 84.0% by weight less than two microns; a residue of about 0.0005% at 325 mesh; a moisture content of about 0.5%; a slurry solids of about 67.5%; and a Brookfield slurry viscosity of about 325 cps @ 20 rpm. Generally, these measurements were taken using TAPPI approved methods.

Reference may be made to U.S. Patent No. 5,085,707 for a further discussion of the commercial clays, including the ASTRA-PLATE® product. Other examples of a platy kaolin clay which may be used in the invention are the ASTRA-FIL® 90 and ASTRA-FIL® clays, which are also marketed as a commercial clay by the aforesaid assignee of the present application, and both are declaminated kaolin clays.

The "fine" particle size distribution of the platy kaolin clay used in the invention may be considered as being at least 80% by weight less than two microns in equivalent spherical diameter (e.s.d.)..

Calcination is a process which subjects the crude kaolin clay to a temperature of about 500°C to convert the kaolinite into a different form referred to as "metakaolin". The calcination process causes particles to "stick" or "fuse" together into porous aggregates and results in a pigment with high light scatter caused by 1) higher index of refraction and 2) higher amount of light scattering surface. When a clay is uncalcined (hydrous) it means that it has not been subjected to a heat treatment.

-10-

Anhydrous (calcined) white kaolin clay pigments are useful as a coating and as a filler in paper products. An example of such a product is disclosed in U.S. Patent No. 4,381,948 to McConnell et al. presently assigned to ECC

5 International Inc. Generally, the paper products to which these pigments relate are structured particles with low aspect ratios, such as that below 30, and which product may not be as effective for use in the invention in view of its low aspect ratio.

10 Delamination as used herein refers to the operation of subjecting the naturally occurring kaolin stacks in the aqueous clay slurry to shearing forces which may be produced by the shearing action of a sand grinder, thereby reducing the kaolin stacks to thin platelets to produce individual  
15 particles having an equivalent spherical diameter less than 2 microns. Instead of a sand grinder, delamination may be carried out in other devices such as, ball or pebble mills, extruders or rotor-stator colloid mills. Reference may be made to U.S. Patent No. 3,615,806 for a thorough discussion of  
20 the process of delamination of kaolin clay.

The term "defining" generally refers to the operation of separating and discarding a percentage of the fine fraction of the kaolin suspension. The defining operation may be carried out on a centrifuge where the kaolin suspension to be  
25 "defined" is supplied to the centrifuge and processed therein to separate the suspension into a coarse fraction and a fine fraction. A selected percentage by volume of the fine fraction is discarded, while the remainder of the fine fraction is admixed with the coarse fraction for further processing.  
30 Defining to a level of 40% means that 40% of the fine fraction from the centrifuge was discarded and the remaining 60% of the fine fraction from the centrifuge was admixed with the coarse fraction from the centrifuge for further processing.  
Reference may be made to U.S. Patent No. 4,943,324 for a

-11-

further discussion of the delamination and the defining processes.

When a clay is "undefined", needless to say, the clay has not undergone the "defining" process as discussed in the preceding paragraph.

In the following examples, the acid resistant calcium carbonate was that prepared according to the teachings of the aforesaid patent application bearing U.S. Serial No. 08/614,863 filed March 13, 1996 which uses sodium aluminate and phosphoric acid to treat the calcium carbonate, and which is incorporated herein by reference. This product is processed by ECC International Inc. under the tradename OPTICAL® NB (neutrally buffered) calcium carbonate. In the practice of the invention, the acid resistant calcium carbonates discussed hereinabove and others which are available in the market place may be used. The platy kaolin clay used in the examples was the aforesaid ASTRA-PLATE® product, which qualifies as being a platy kaolin clay. In the practice of the invention, the platy kaolin clays discussed hereinabove and others available in the market place may be used.

It is believed by the inventors that since the acid resistant precipitated calcium carbonates resist dissociation in an acidic environment, that it can be blended or mixed with a platy kaolin clay for use as a filler composition in an acid made paper in order to increase brightness and opacity and decrease porosity, especially in supercalendered grades of paper. Both of these components for the filler composition of the invention may remain in dry form or may be slurried, and blended for a sufficiently long period of time to ensure uniform mixing thereof. This filler composition is then added to the stock furnish according to standard practice for adding fillers to the furnish.

In the examples below, percentages of acid resistant precipitated calcium carbonates/ platy kaolin clays for use as

-12-

a filler composition in an acid making process for paper were 25%/75%, 50%/50%, and 75%/25% on a weight basis relative to the percentage of filler used in the paper stock furnish. The percentage of filler in the handsheets ranges from about 1.0% to about 40% based upon the total weight of paper stock furnish and based on the desired fiber weight of the paper.

The invention is further illustrated by the following examples, which are to be considered illustrative of the invention, and not limited to the precise embodiments discussed herein.

#### EXAMPLE 1

A pulp slurry of 80% groundwood and 20% kraft was used as the stock furnish. The groundwood was obtained from Crown Vantage Inc., St. Francisville, Louisiana, and the kraft was obtained from the Potlatch Corporation, Cloquet, Minnesota. A blended slurry (20% solids) of 25% of the OPTICAL<sup>®</sup> NB acid resistant calcium carbonate product and 75% of the ASTRA-PLATE<sup>®</sup> kaolin clay product was made and added to the paper stock furnish as a filler. The stock was kept at a pH of 7.0 during the course of the experiment by adding 1% sulfuric acid solution or 25% caustic solution.

A retention aide available under the tradename Hydrad TRP 954, which is a cationic emulsion copolymer manufactured by the Calgon Corporation, Pittsburgh, PA was used in order to improve the retention of the filler composition. Generally, the retention of the filler in the final product is between 50% to 80% of the initial amount added to the base stock. Handsheets were made using a British handsheet mold known to those skilled in the art. The sheets were pressed twice in order to squeeze out as much water as possible, and dried in a drum drier. The grammage, which is known in the art as being a measurement of the basis weight of a sheet of paper, of each handsheet was kept around 60 grams per meter, and the formation of each handsheet was kept around 175 as measured by the OpTest, which is an instrument made by OpTest Instruments,

-13-

Inc. As is known, the formation is characterized as being the physical distribution and orientation of fibers and other solid constituents in the structure of a sheet of paper that effects its appearance and other physical properties. A  
5 formation having a 175 value is generally considered as being "good formation." The sheet was then supercalendered by a laboratory calender machine manufactured by Beloit Wheeler Co. at 1500 psi through 5 nips at 150° C. One nip is defined as the contact area between the two rolls of the calender  
10 machine.

#### EXAMPLE 2

The procedure for producing handsheets was followed as described in Example 1 except that the filler blend composition comprised 50% of the OPTICAL® NB calcium carbonate  
15 product and 50% of the ASTRA-PLATE® kaolin clay product.

#### EXAMPLE 3

The procedure for producing several handsheets was followed as described in Example 1 except that the filler blend composition comprised 75% of the OPTICAL® NB calcium  
20 carbonate product and 25% of the ASTRA-PLATE® kaolin clay product.

For comparison purposes, additional handsheets were prepared in a manner similar to that for Examples 1, 2, and 3. These additional handsheets are designated in the Figures 1-7  
25 as "Blank", which means that the handsheets had no fillers; as "Optical NB", which means the filler composition consisted only of acid-resistant calcium carbonate; and as "Astra-Plate", which means that the filler consisted only of a platy kaolin clay.

30 The optical properties of these several handsheets for these six (6) different categories were measured in the paper testing laboratory of ECC International Inc. in their Sandersville, Georgia plant. The results are shown in Figures 1 through 7.

-14-

In Figures 1-7, the properties for the several handsheets in the six categories are plotted as a function of percent ash, where ash equals the total percentage of filler loading at 500°C in the paper. The handsheets were tested for opacity, brightness, and total filler content by ashing, using TAPPI standard test methods. The handsheets were made with the filler added to the paper stock furnish and then burned at 500°C. The percent ash is the ash weight over the sheet weight times 100 percent. Figures 1 and 2 show the TAPPI brightness and TAPPI opacity values, respectively. The brightness and opacity values for the blended filler composition of Example 3, i.e. 75% acid-resistant precipitated calcium carbonate and 25% platy kaolin clay, were superior to at least the blended filler compositions of Example 1 (25% OPTICAL® NB product/75% ASTRA-PLATE® product) and Example 2 (50% OPTICAL® NB product/50% ASTRA-PLATE® product), and essentially equivalent to the handsheet containing the single acid resistant calcium carbonate or the OPTICAL® NB product.

The Gurley porosity values for the six categories of handsheets are plotted in Figure 3. The handsheets which offered the higher Gurley porosity values when considered over the range of % ash for each kind of handsheet, and therefore the less porous, were the ones that contained either the ASTRA-PLATE® filler or the blends of filler composition of the invention. The handsheets with the lower Gurley porosity values, and therefore higher porosity, were the ones containing the single acid resistant calcium carbonate (OPTICAL® NB product). These results show that the handsheets with the platy clay or the filler blends of the invention are less porous when compared to the other categories of handsheets.

Figures 1-3 show that the brightness and opacity for the handsheets containing the filler composition of the invention, particularly that containing 75% acid resistant calcium carbonate and 25% kaolin clay, are at least equivalent to the



-15-

handsheets containing only the acid resistant calcium carbonate filler, and that the porosity for the handsheets containing the filler composition of the invention is lower than that containing only the acid resistant calcium carbonate as a filler in the paper stock furnish.

Figures 4 through 6 show formation, caliper (thickness), and bulk values for the six categories of handsheets. The formation values were obtained through the OpTest method, and the caliper and bulk values were obtained through the approved TAPPI methods for measuring thickness and bulk. The results plotted in Figures 4-6 demonstrate that the formation, the caliper, and the bulk of the handsheets for the six categories were essentially the same and were not significantly different for the handsheets processed according to the teachings of the present invention.

Figure 7 shows the sheet gloss for the several handsheets of the six categories. The gloss values were obtained through the TAPPI method for measuring sheet gloss. From Figure 7, it can be seen that the gloss values for the handsheet containing the fillers of both the prior art and the invention were also approximately the same for the same percentage of filler. Whereas, the blank handsheets or the ones that did not contain a filler were relatively lower than those that did contain a filler, whether or not the filler was in accordance with the teachings of the present invention.

A second part of the experiment for the present invention involved a pilot paper machine trial which was done in an attempt to substantiate the findings of the preceding examples.

#### Pilot Paper Machine Trial

Paper was made on a laboratory scale on a papermaking machine. The machine was a Bel Baie IV machine which is manufactured by the Beloit Corporation. This machine includes a Bel-Baie twin-wire machine; a Foundrinier; a press section; and a dryer section. The trial was conducted at the Beloit

-16-

Corporation Research and Development Center. The stock was a repulped newsprint, which is a groundwood-containing paper grade, obtained from Fletcher Challenge Company, which is a newsprint manufacturer located in western Canada. The grade  
5 was a 45 grams per meter newsprint. Four categories of handsheets were prepared. These included 1) unfilled; 2) an acid resistant precipitated calcium carbonate (OPTICAL® NB) filler only; 3) a blend filler composition of the present invention which was 75% acid resistant precipitated calcium  
10 carbonate (OPTICAL® NB) and 25% platy kaolin clay (ASTRA-PLATE®); and 4) a platy kaolin clay (ASTRA-PLATE®) filler only.

A retention aide and a formation aide were added to the stock slurry. The retention aide was Eclipse® 200 which is a water soluble polymer and the formation aide was Stylus™ 100,  
15 which is a lignosulfonate. These aids were added in typical amounts of about 0.2 to 0.3 lbs./ton and in a conventional manner. These products are provided by the Calgon Corporation, Pittsburgh, PA. The pH of the stock was maintained at 6.5 at the headbox by adding a solution of 10%  
20 phosphoric acid or of 10% sulfuric acid to the tray water.

The caliper of the paper was maintained between 85 to 88 microns, and the formation was around 12 (NUI) or a 65 Kajaani Index, which are typical measurement units. The paper was calendered by a soft nip calender machine in line with the  
25 paper machine.

The results of the paper obtained from the trial are plotted in Figures 8 through 14 for the four categories. The loading filler level in the paper was kept at 5%.

Figures 8 and 9 show the brightness and opacity values  
30 which were obtained through standard TAPPI methods. As these figures show, the brightness and opacity values for the paper having the filler blend of the present invention, i.e. the blend of 75% of the OPTICAL®NB product and 25% of the ASTRA-PLATE® product as a filler, are essentially equal to the paper  
35 having only the acid resistant calcium carbonate OPTICAL® NB

-17-

product as a filler, but are higher than the other kinds of papers.

As Figures 10 and 11 show, the tensile index values of the paper having the filler blend of the present invention appear to be higher than the paper having the OPTICAL® NB product as a filler. These tensile index values were obtained by using a tensile tester made by Thwing Albert (Intelect II-Std.).

Figures 12 and 13 show that the sheets made with 5% clay loading and with the 5% loading of the 75%/25% blend were less porous than the other kinds of paper. The porosity values of Figure 12 were obtained by the air permeability method, whereas that of Figure 13 were obtained by the Gurley porosity method. These methods for determining porosity are well known to those skilled in the art. It is also known to by those skilled in the art that the lower values of the air permeability method represents a less porous material, whereas the higher values of the Gurley method represents a less porous material.

Figure 14 shows that the gloss values for all four kinds of paper including that containing the filler composition of the present invention were about the same. These gloss values were obtained by the standard TAPPI method for measuring gloss.

As can be seen from the above results shown in Figures 8-14, the handsheets and/or paper containing the filler composition of the invention, and in particular, 75% acid resistant precipitated calcium carbonate and 25% the platy kaolin clay, had brightness and opacity values at least comparable to those having either the filler with only the acid resistant precipitated calcium carbonate or with only the platy kaolin clay, and was less porous than those having only the acid resistant precipitated calcium carbonate filler.

From this, it can be concluded that the filler of the present invention, involving the mixture of a platy kaolin clay and an

-18-

acid resistant precipitated calcium carbonate, may have the best properties of both pigments, that is, the precipitated calcium carbonate and the platy clay.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations et reside within the scope of the present invention. Accordingly, the invention is to be broadly construed and limited only by the scope and spirit of the claims now appended hereto.

-19-

WHAT IS CLAIMED IS:

1. A filler composition for a groundwood containing grade of paper, comprising:  
an effective amount of an acid resistant precipitated calcium carbonate and an effective amount of a platy kaolin clay which is added to the paper stock furnish to produce a final paper product exhibiting improved properties.
2. A filler composition of Claim 1 wherein said effective amount of said acid resistant precipitated calcium carbonate is from about 5% to about 95%, by weight, per amount of said filler composition and wherein said effective amount of said platy kaolin clay is from about 5% to about 95%, by weight, per amount of said filler composition.
3. A filler composition of Claim 1, wherein said filler composition ranges from about 1.0% to about 40%, by weight, based upon the total weight of said paper stock furnish.
4. A filler composition of Claim 1 wherein said effective amount of said acid resistant precipitated calcium carbonate is about 25% to about 75%, by weight, per amount of said filler composition and wherein said effective amount of said platy kaolin clay is about 25% to about 75%, by weight, per amount of said filler composition.
5. A filler composition of Claim 1 wherein said groundwood containing grade of paper is made under acidic conditions, and is calendered or supercalendered.
6. A process for producing a paper web, the steps comprising:  
forming a web of papermaking fibers including groundwood pulp and a filler composition comprising an effective amount of an acid resistant precipitated calcium

-20-

carbonate and an effective amount of a platy kaolin clay to produce an acid type final product.

7. A process of Claim 6 wherein said effective amount of said acid resistant precipitated calcium carbonate is from about 5% to about 95%, by weight, per amount of said filler composition and said effective amount of said platy kaolin clay is from about 5% to about 95%, by weight, per amount of said filler composition.

8. A process of Claim 6 wherein said effective amount of said acid resistant precipitated calcium carbonate is about 25% to about 75%, by weight, per amount of said filler composition and said effective amount of said platy kaolin clay is about 25% to about 75%, by weight, per amount of said filler composition.

9. A method of improving the properties of an uncoated paper product comprising adding a filler composition of Claim 1 to the papermaking fibers at least prior to the preparation of a web for producing said paper product.

10. A method of Claim 9 wherein said effective amount of said acid resistant precipitated calcium carbonate is from about 5% to about 95%, by weight, per amount of said filler composition and wherein said effective amount of said platy kaolin clay is from about 5% to about 95%, by weight, per amount of said filler composition.

11. A method of Claim 9 wherein said effective amount of said acid resistant precipitated calcium carbonate is about 25% to about 75%, by weight, per amount of said filler composition and wherein said effective amount of said platy kaolin clay is about 25% to about 75%, by weight, per amount of said filler composition.

-21-

12. An improved paper product comprising the filler composition of Claim 1.

13. A product of Claim 12 wherein said effective amount of said acid resistant precipitated calcium carbonate is from about 5% to about 95%, by weight, per amount of said filler composition and wherein said effective amount of said platy kaolin clay is from about 5% to about 95%, by weight, per amount of said filler composition.

14. A product of Claim 12 wherein said effective amount of said acid resistant precipitated calcium carbonate is about 25% to about 75%, by weight, per amount of said filler composition and wherein said effective amount of said platy kaolin clay is about 25% to about 75%, by weight, per amount of said filler composition.

15. A product of Claim 12 wherein said filler composition ranges from about 1.0% to about 40.0%, by weight, based upon the total weight of said paper stock furnish.

16. A product of Claim 12 wherein said paper product has at least a brightness ranging from about 70% to 80% and an opacity of about 85% to about 95%.

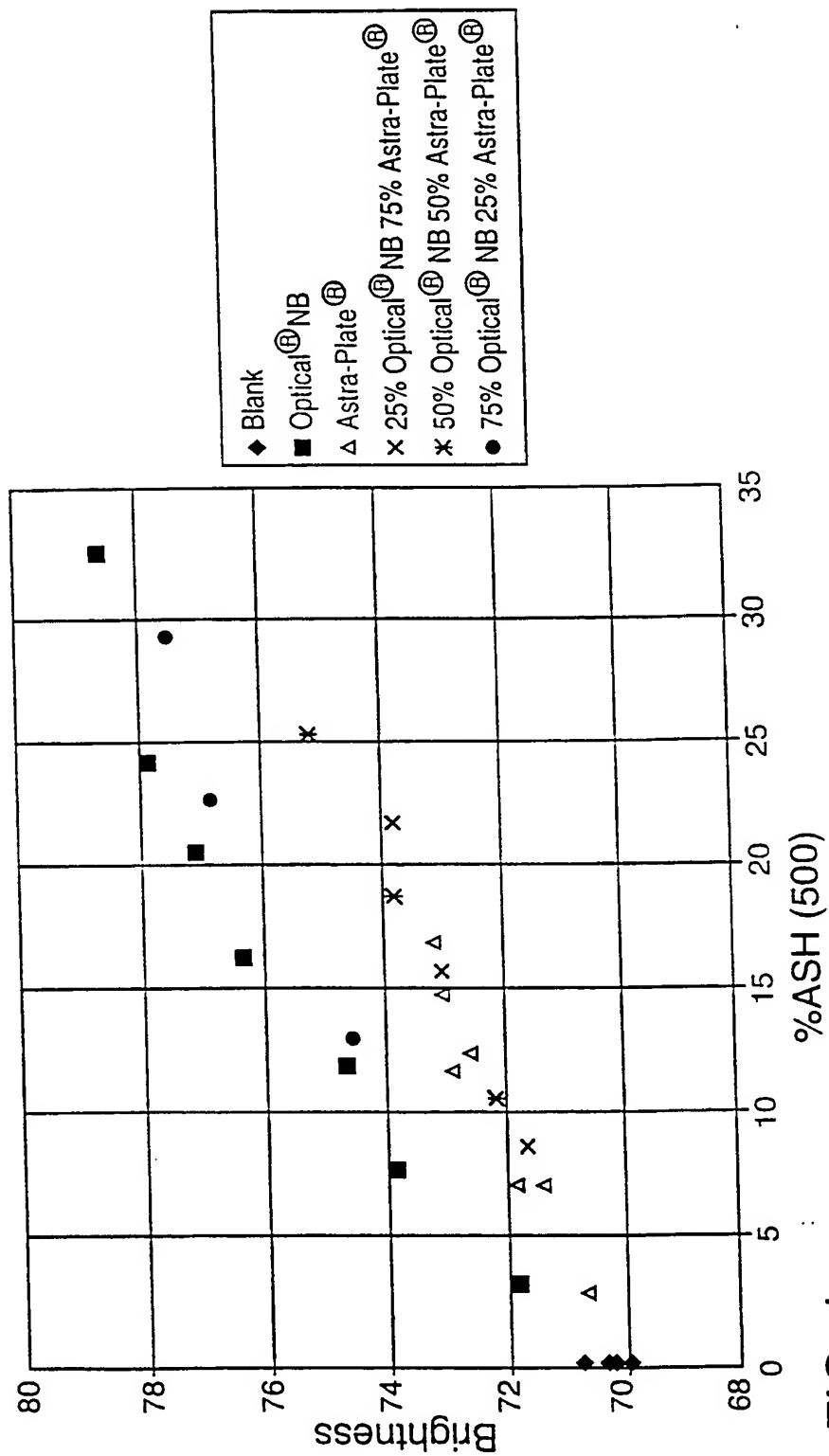
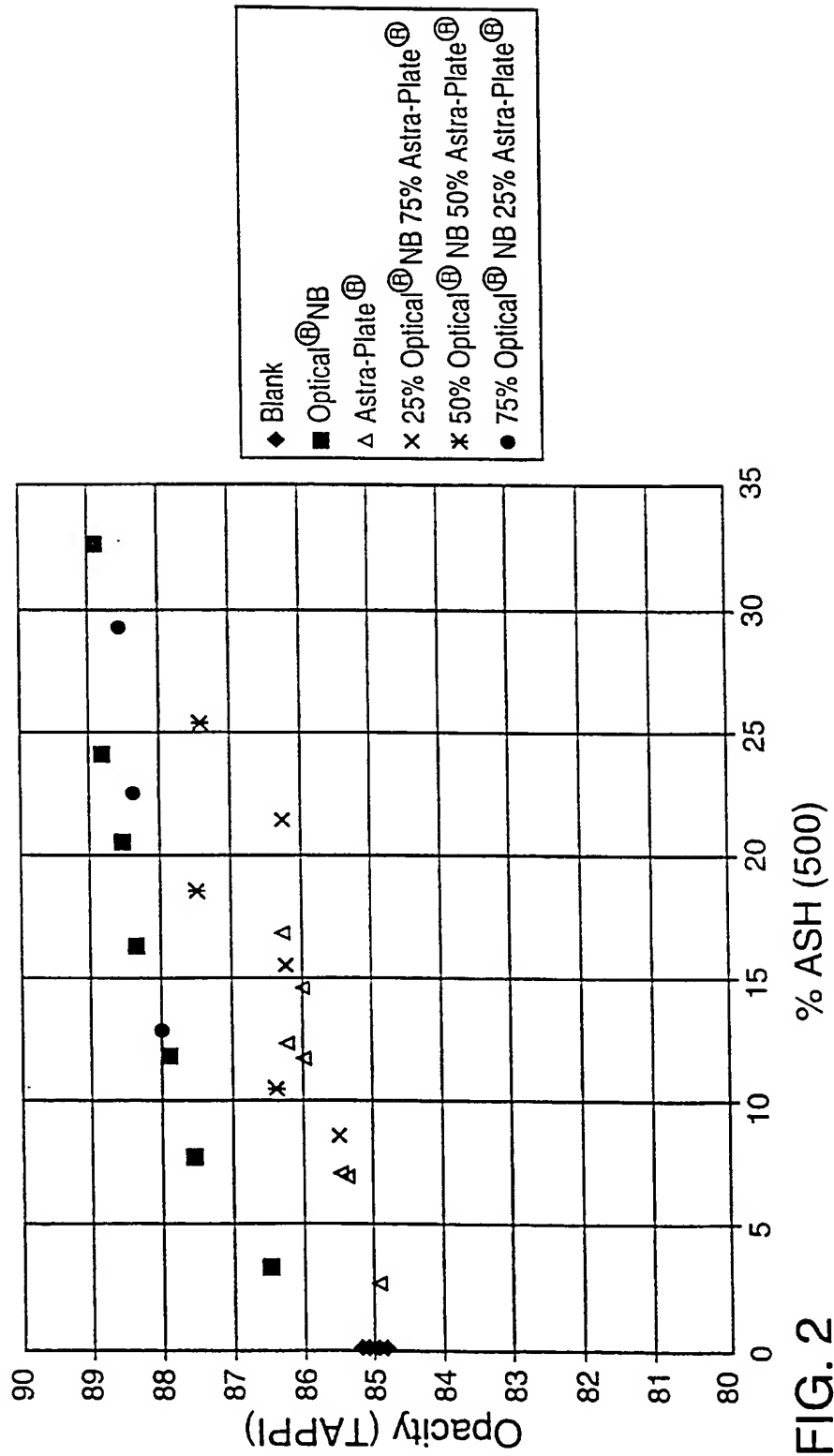


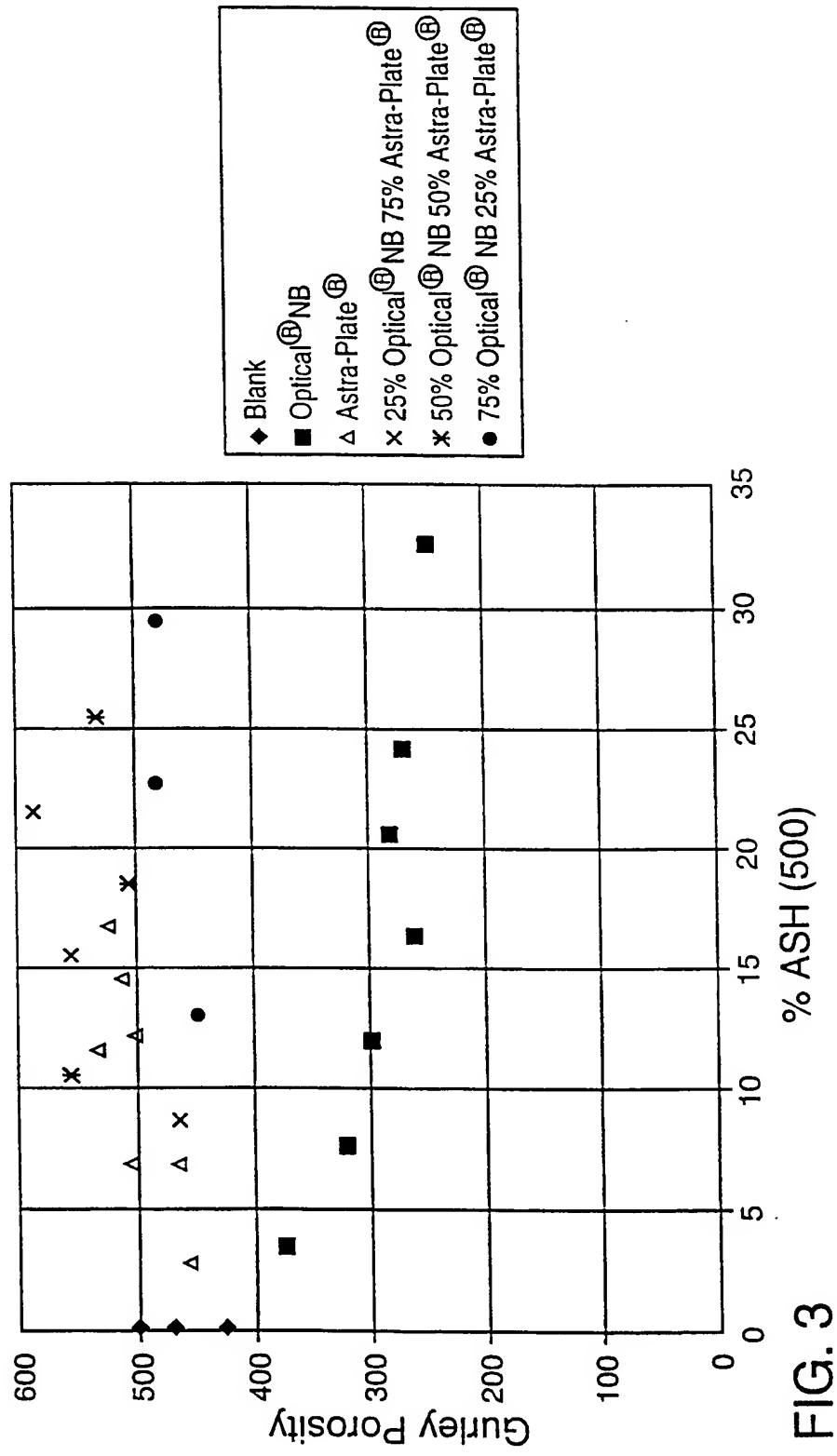
FIG. 1



2/14



3/14



4/14

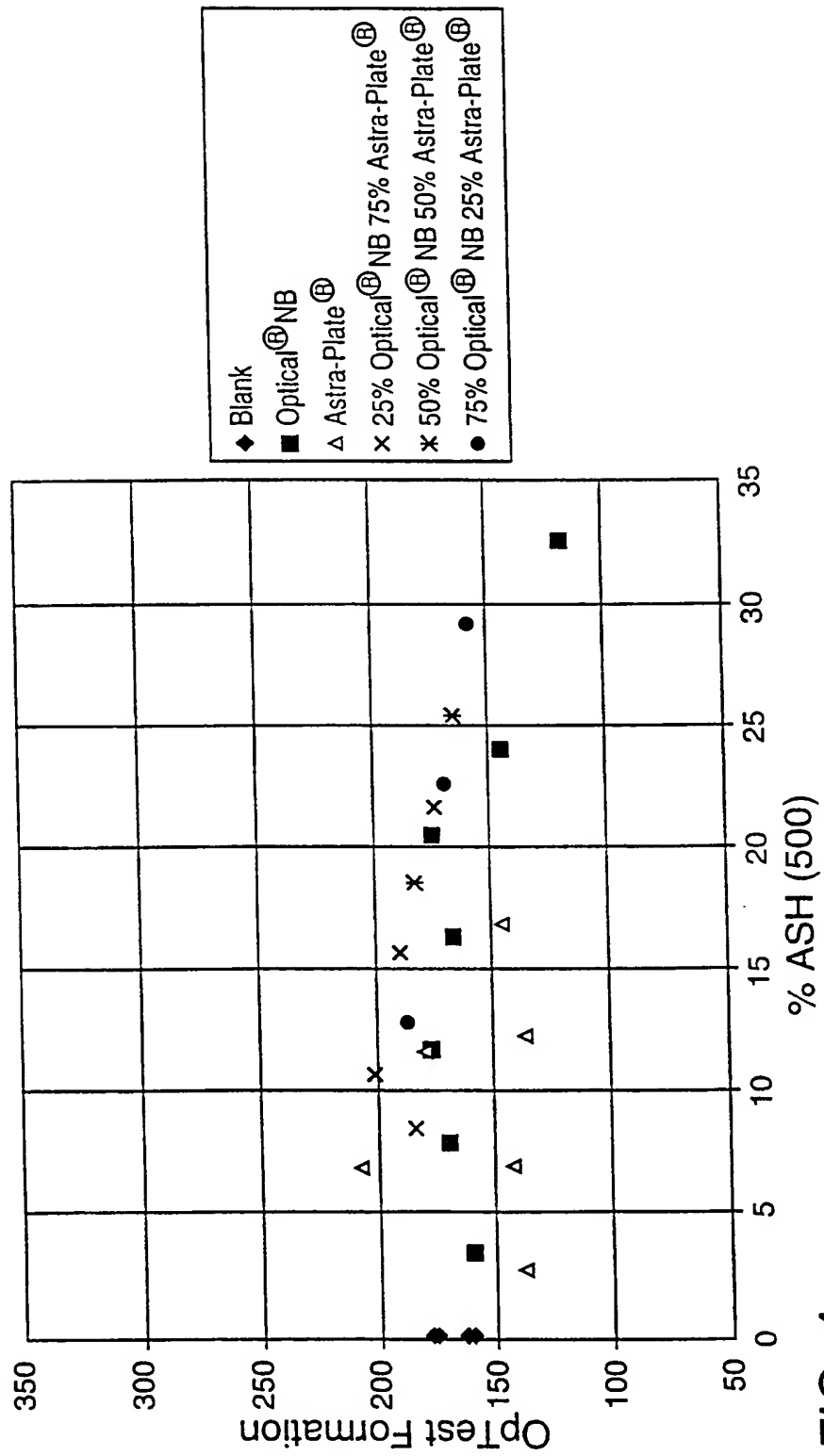


FIG. 4

5/14

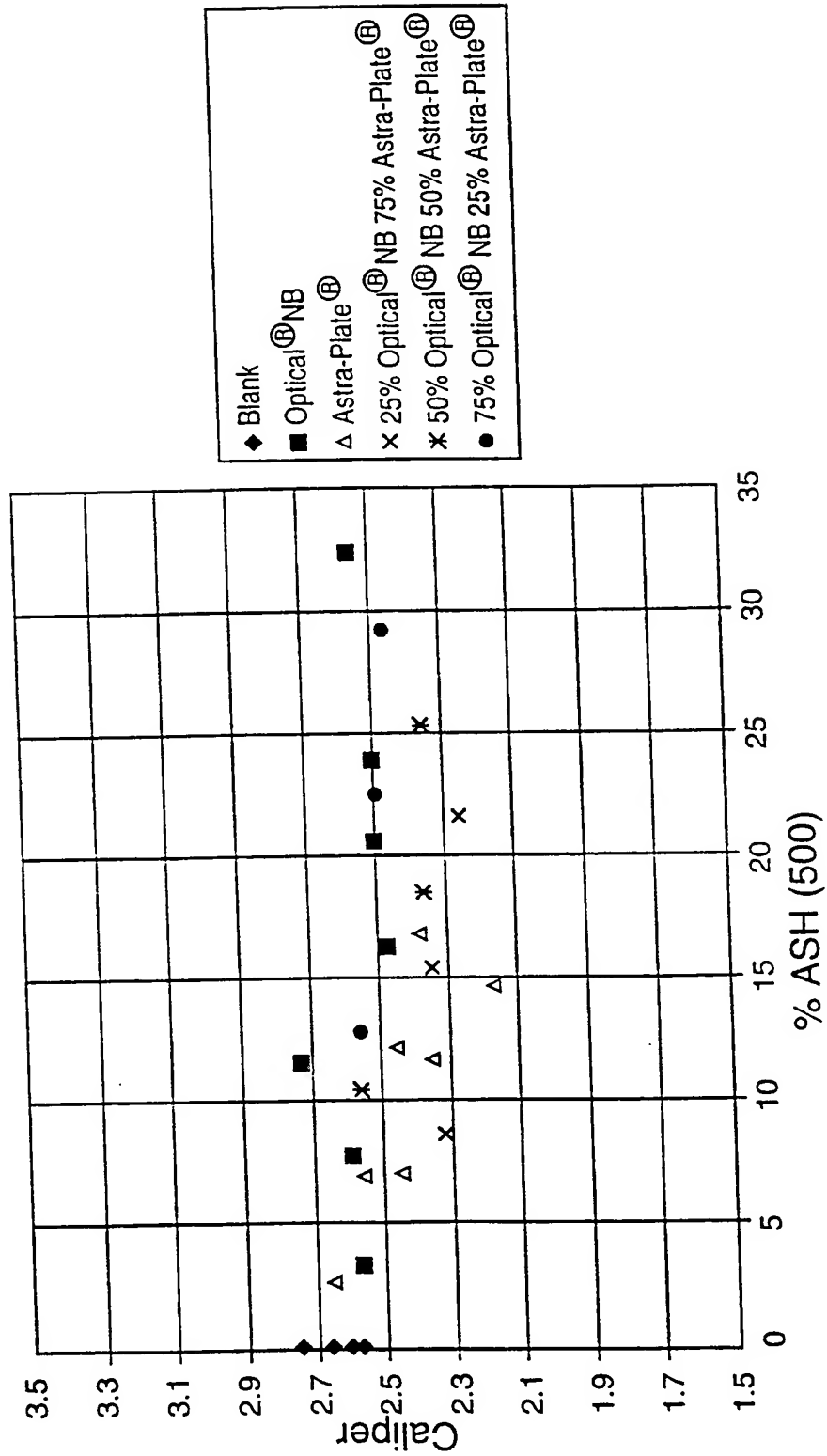


FIG. 5

.6/14

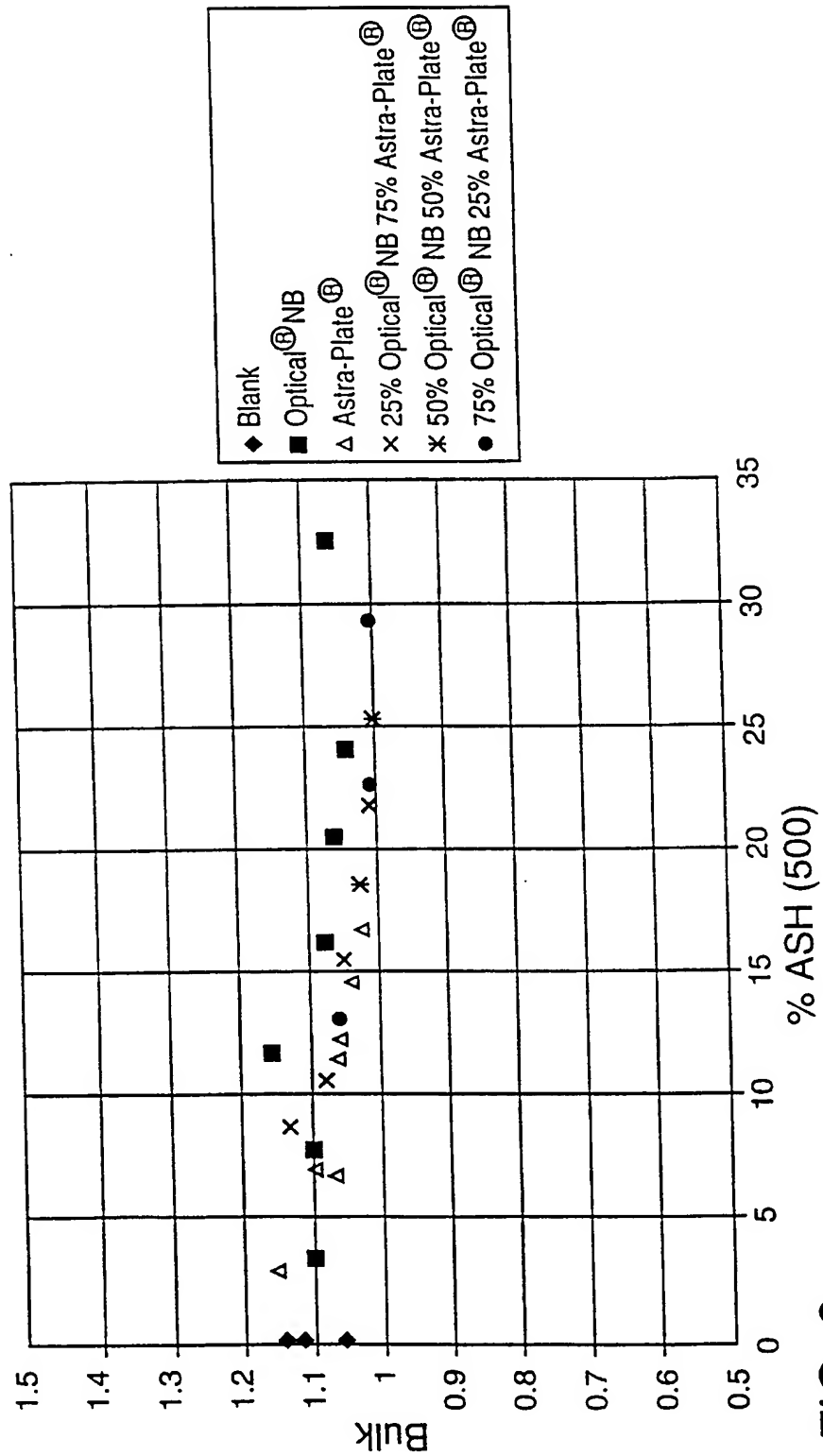


FIG. 6

7/14

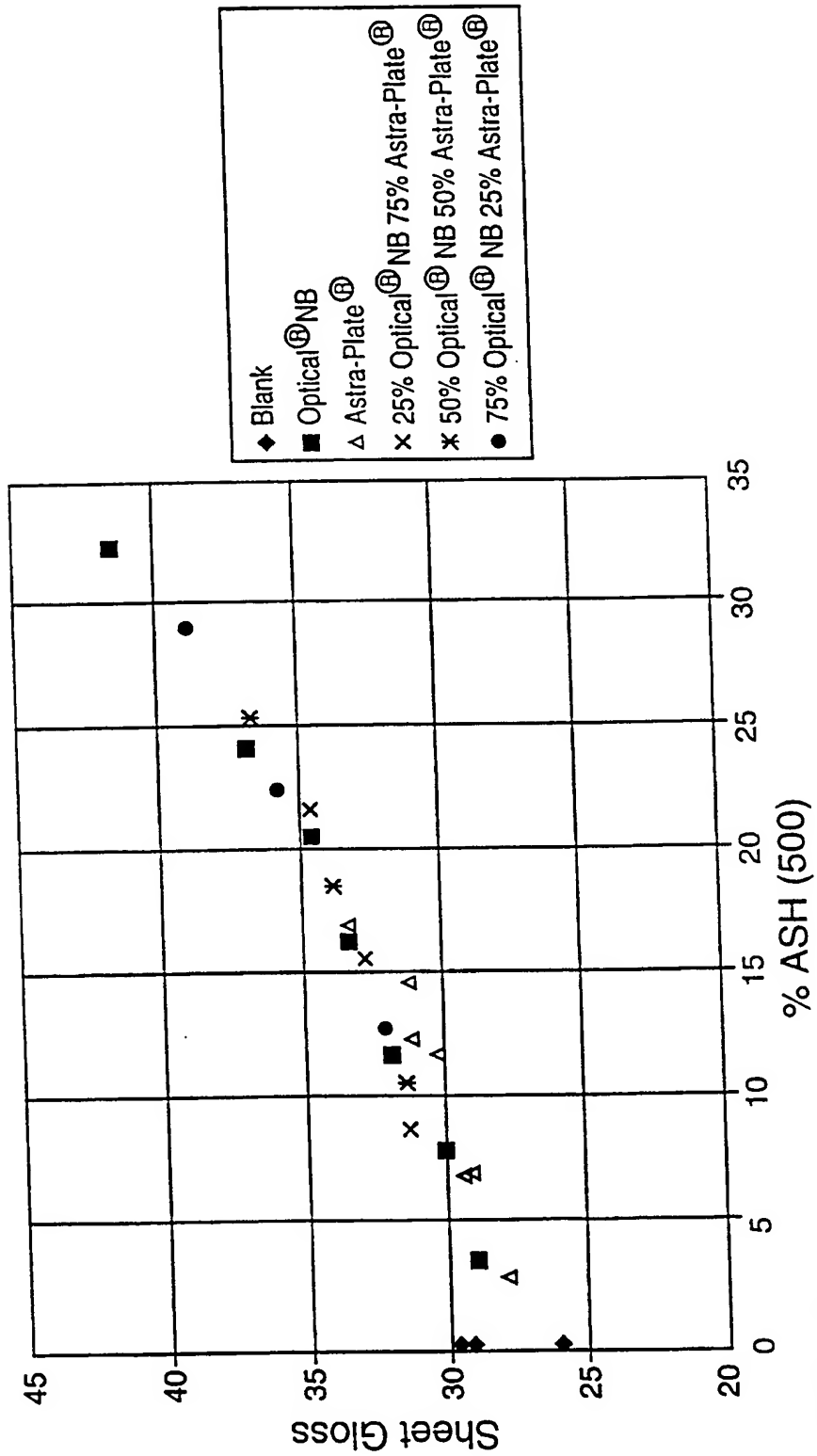


FIG. 7

8/14

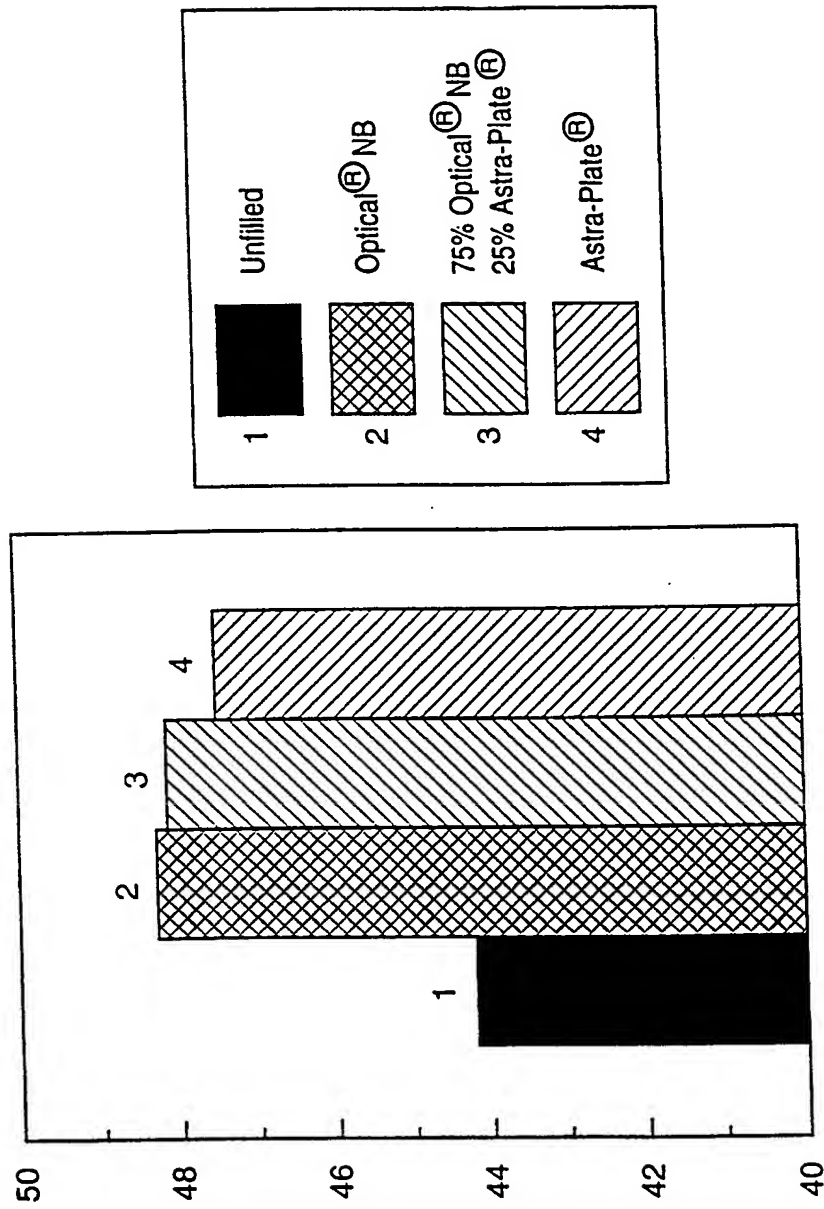


FIG. 8

9/14

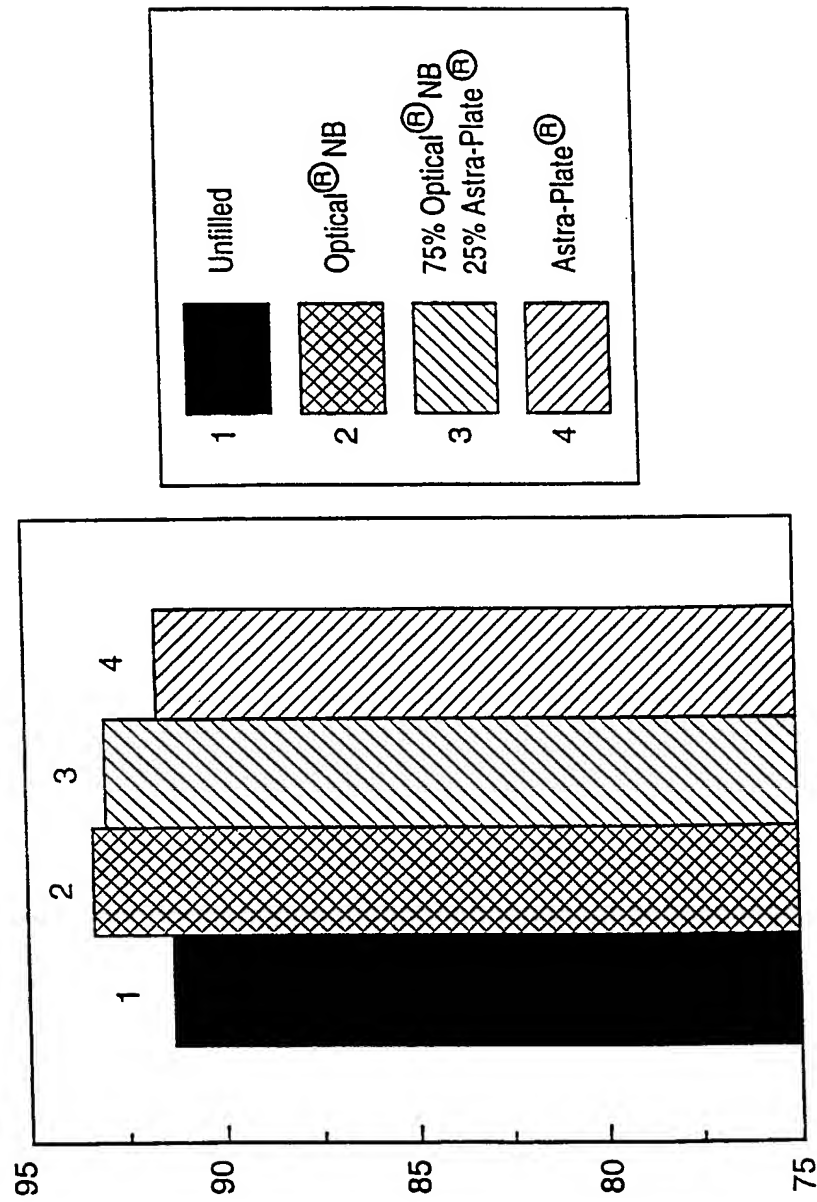


FIG. 9



10/14

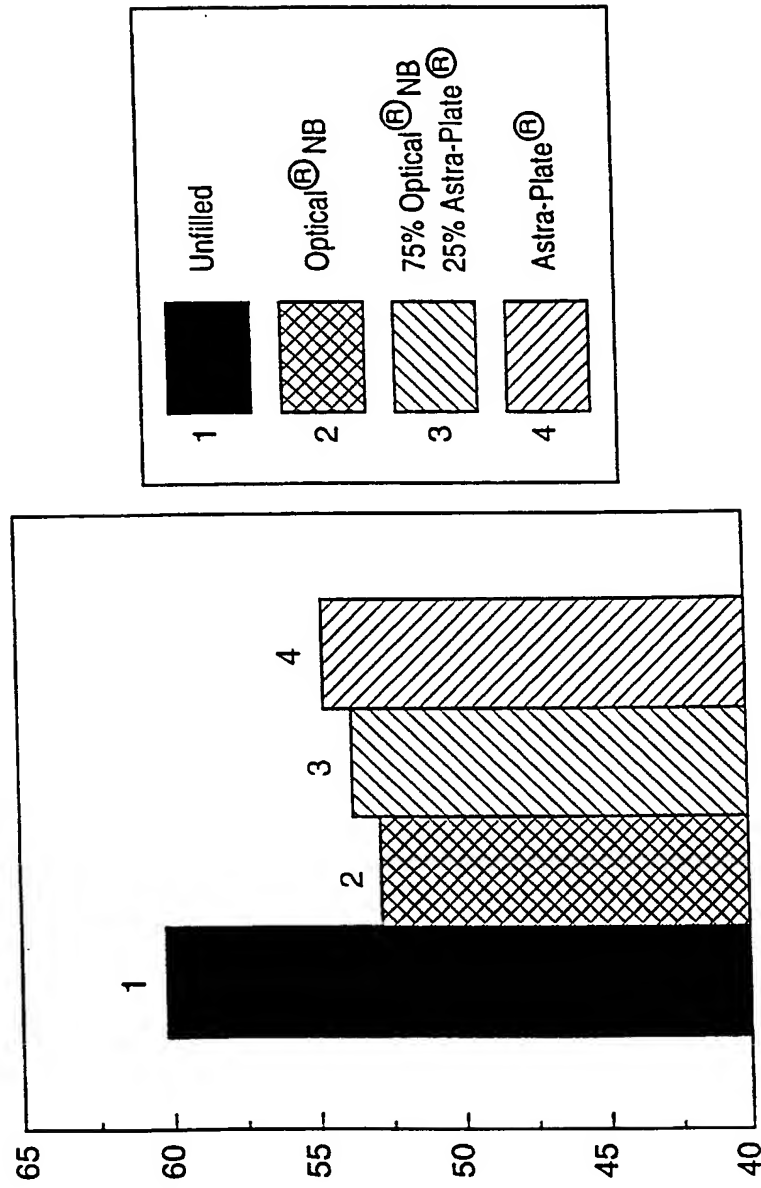


FIG. 10

11/14

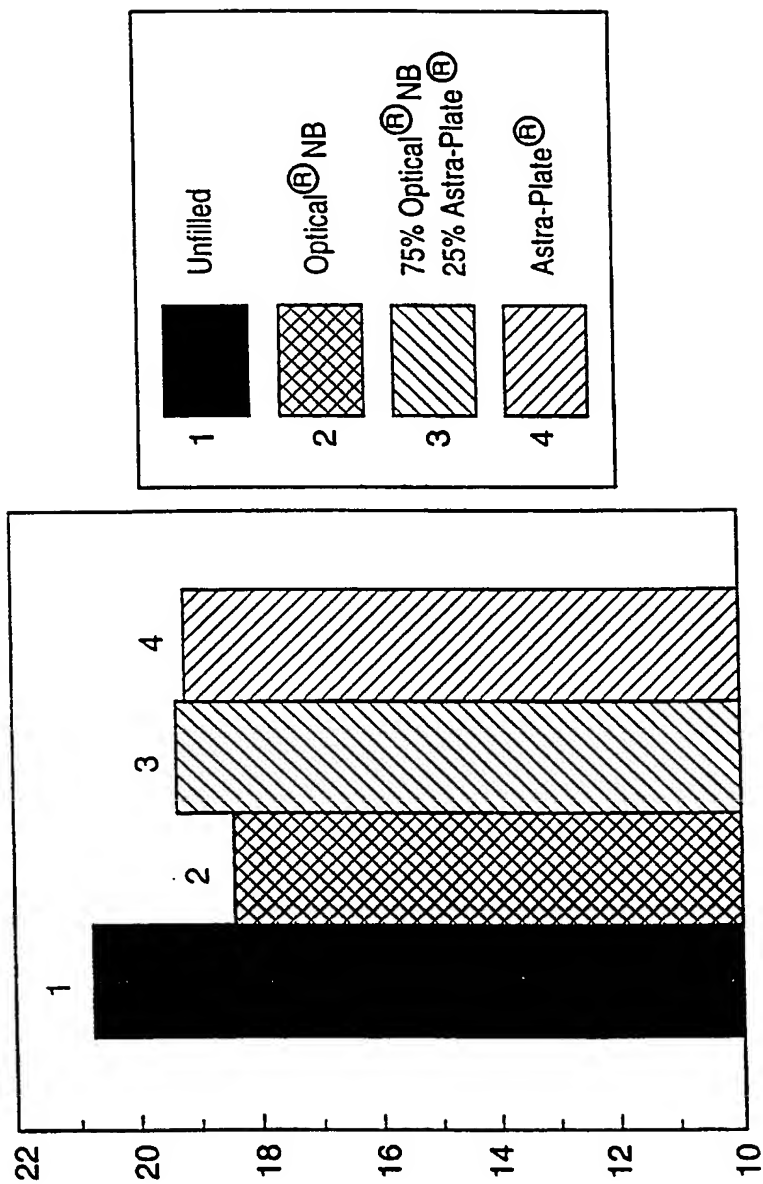


FIG. 11

12/14

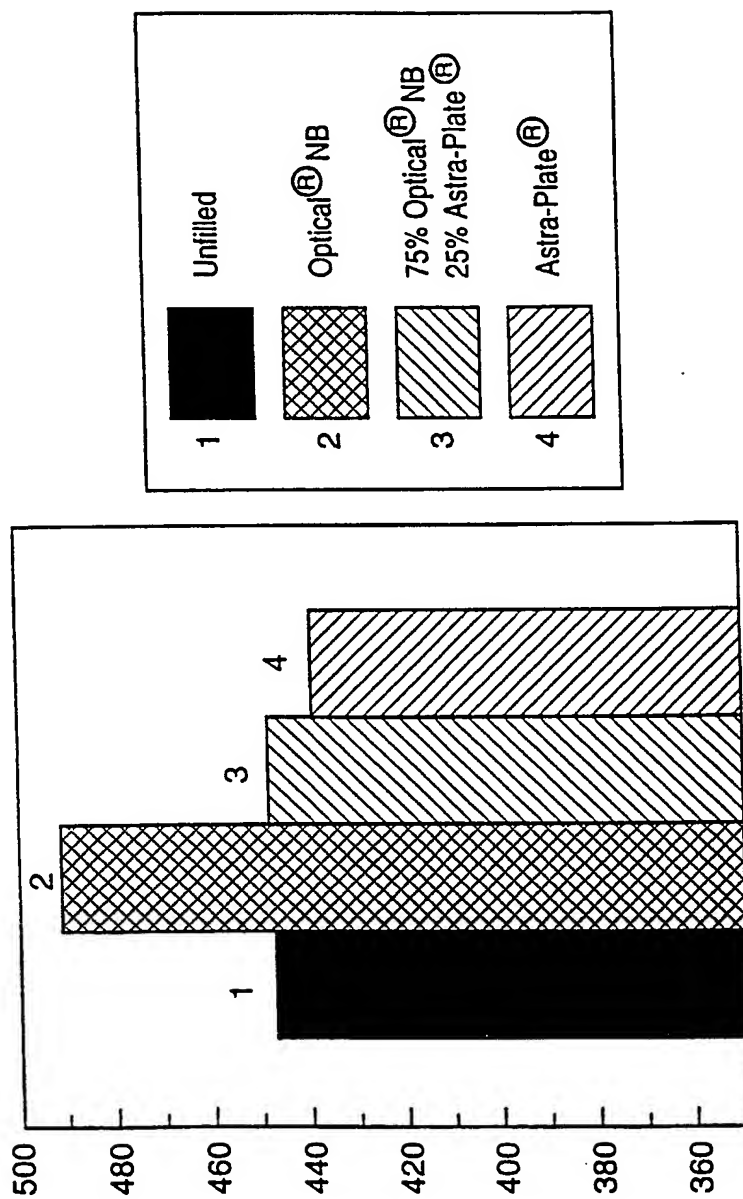
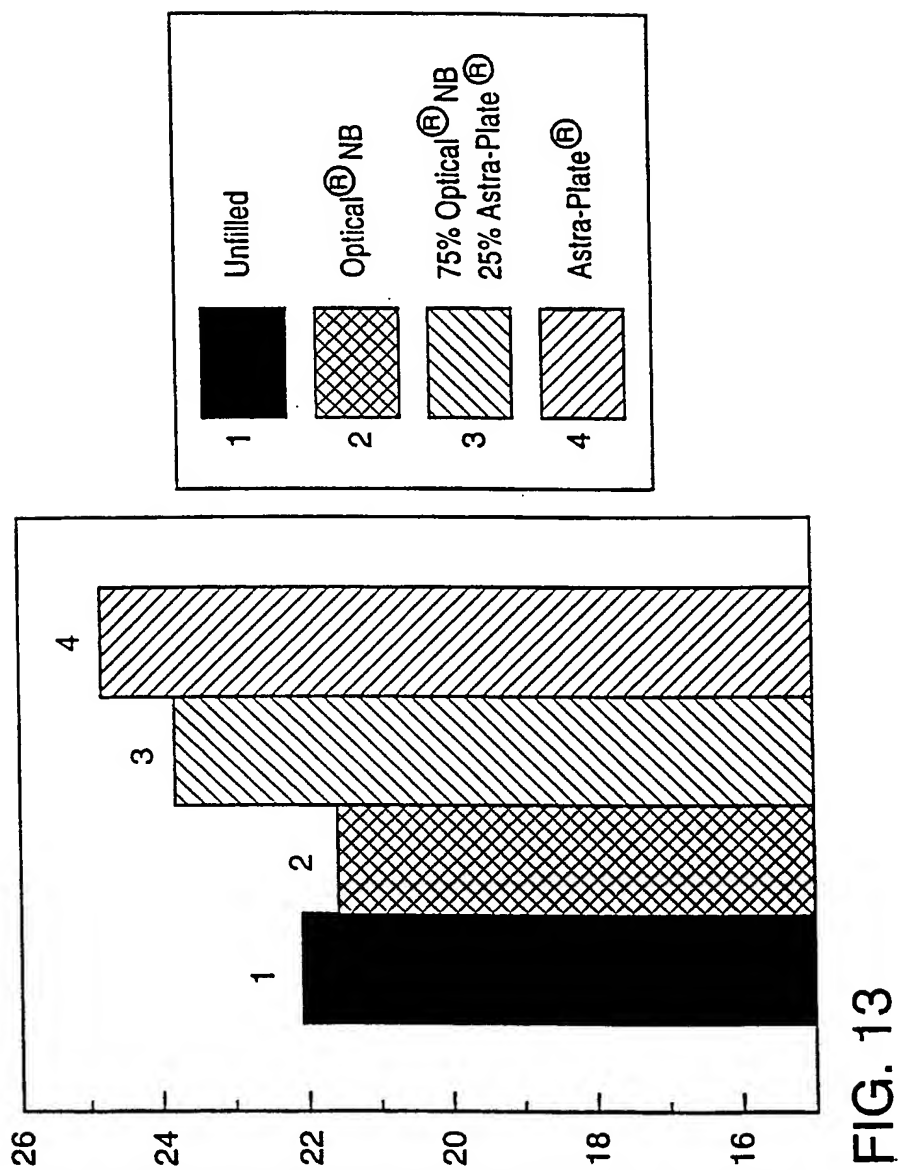


FIG. 12

13/14



14/14

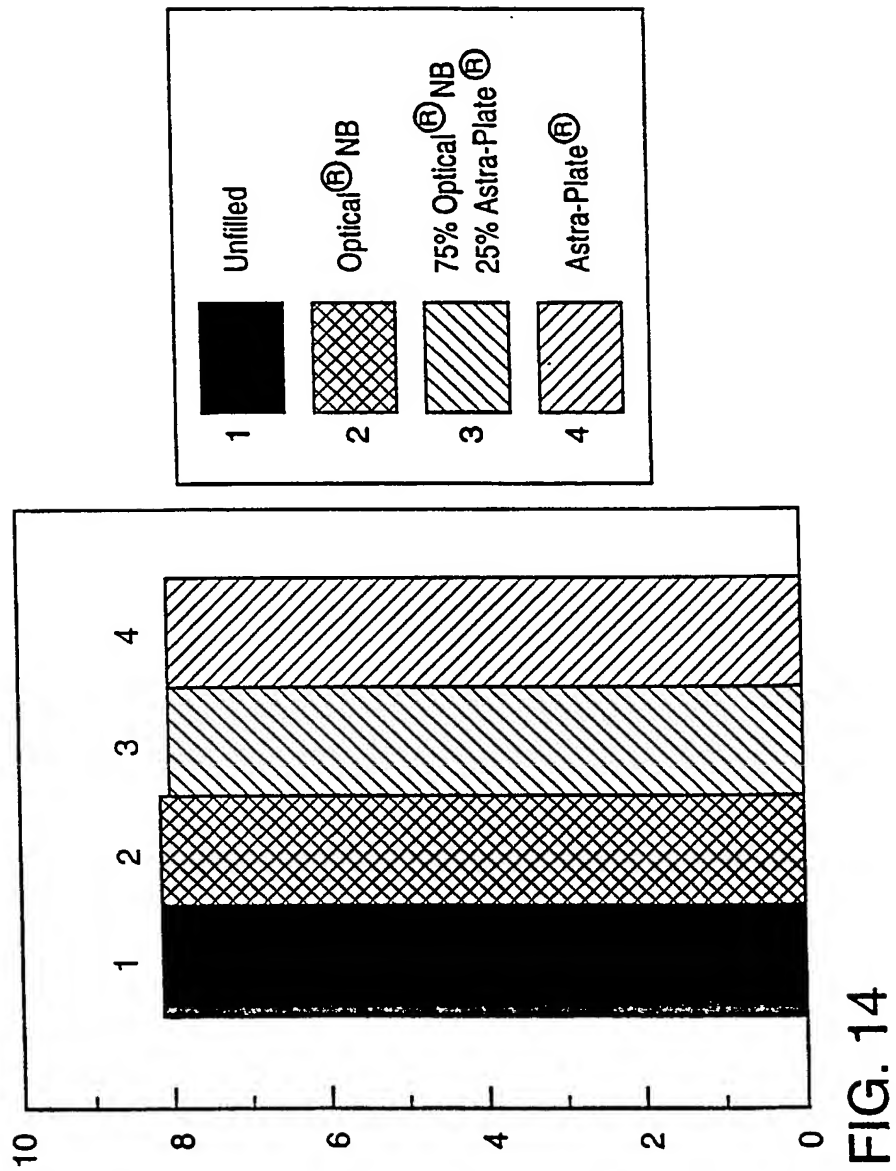


FIG. 14

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/11626

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/181.2, 181.1, 181.7, 181.8, 135; 106/401, 464, 486, 416; 427/391, 361

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG, APS

Search terms: groundwood, paper?, delaminated kaolin, platy kaolin, calcium carbonate

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,943,324 A (BUNDY et al) 24 July 1990 (24-07-90), see entire document.	1-16
Y	US 5,531,821 A (WU) 02 July 1996 (02-07-96), see the whole document.	1-16
A	US 5,292,365 A (DELFOSSE) 08 March 1994 (08-03-94), see whole document.	1-16
A	US 4,927,498 A (RUSHMERE) 22 May 1990 (22-05-90), see entire document.	1-16

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*B* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

02 SEPTEMBER 1998

Date of mailing of the international search report

02 OCT 1998

 Name and mailing address of the ISA/US  
 Commissioner of Patents and Trademarks  
 Box PCT  
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOSE A. FORTUNA

Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/11626

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (6):

C09C 1/02, 1/42, 1/62, 1/64; C04C 14/00; D21H 17/64, 17/68, 17/63, 17/67

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

162/181.2, 181.1, 181.7, 181.8, 135; 106/401, 464, 486, 416; 427/391, 361

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**